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(11) (A) No. 1 260 159

(45) ISSUED 890926

(52) CLASS 356-123  
C. R. CL. 356-128

<sup>4</sup>  
(51) INT. CL. H01L 49/00,  
G01N 27/04, H01G 7/00

(19) (CA) **CANADIAN PATENT** (12)

(54) Molecule-Based Microelectronic Devices

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(21) APPLICATION No. 573,227

(22) FILED 880727

(62) DIV'N OF APPL'N No. 495,996 FILED 851122

(30) PRIORITY DATE (US) U. S. A. (674,410) 841123

No. OF CLAIMS 8

**Canada**

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CCA-274 (11-82)

#### ABSTRACT OF THE DISCLOSURE

1                   Several types of new microelectronic devices  
including diodes, transistors, sensors, surface energy  
storage elements, and light-emitting devices are  
disclosed. The properties of these devices can be  
5                   controlled by molecular-level changes in electroactive  
polymer components. These polymer components are formed  
from electrochemically polymerizable material whose  
physical properties change in response to chemical  
changes, and can be used to bring about an electrical  
10                  connection between two or more closely spaced  
microelectrodes. Examples of such materials include  
polypyrrole, polyaniline, and polythiophene, which respond  
to changes in redox potential. Each electrode can be  
individually addressed and characterized electrochemically  
15                  by controlling the amount and chemical composition of the  
functionalizing polymer. Sensitivity of the devices may  
be increased by decreasing separation between electrodes  
as well as altering the chemical environment of the  
electrode-confined polymer. These very small, specific,  
20                  sensitive devices provide means for interfacing electrical  
and chemical systems while consuming very little power.

1                   This application is a division of application  
serial number 495,996 filed November 22, 1985.

Background of the Invention

5                   Presently available solid state microelectronic  
devices consist of microcircuits with discrete circuit  
elements such as monolithic integrated circuits,  
transistors, diodes, resistors, capacitors, transformers,  
and conductors mounted on an insulating substrate. Thin  
10 film hybrid microcircuits are formed by vapor deposition  
of conductors, such as copper and gold, and resistors,  
such as tantalum, nichrome, and tin oxide onto a passive  
or insulating substrate such as silicon dioxide. An exact  
conductor pattern is obtained by masking or  
15 photolithographic etching. The entire circuit is  
subsequently encased with an epoxy dip to protect against  
moisture and contamination.

Modern integrated circuit devices, even highly  
miniaturized very large scale integrated devices (VLSI),  
20 are responsive only to electrical signals. There is now  
considerable interest in interfacing microelectronic  
devices with chemical and biological systems and it is  
therefore highly desirable to provide a microelectronic  
device that is responsive to such chemical or biological  
25 inputs. Typical applications for these devices include



1 sensing of changes in pH and molar concentrations of  
chemical compounds, oxygen, hydrogen, and enzyme substrate  
concentrations.

5 Applicant is not aware of any apparatus or  
system which allows a direct interface between a  
microelectronic device sensitive to chemical inputs and a  
microminiature electrical circuit. Devices have been made  
on a larger scale which are sensitive to chemical input.  
10 These devices include such well known apparatus as pH  
sensors. Work in this area has recently centered around  
the use of electroactive polymers, such as polypyrrole or  
polythiophene. These compounds change conductivity in  
response to changes in redox potential. Recently, a  
polymeric semiconductor field effect transistor has been  
15 disclosed in a Japanese patent, 58-114465. As described  
in this patent, polymers such as trans-polyacetylene, cis-  
polyacetylene, polypyrrole, and polyvinyl phenylene have  
been used as inexpensive substitutes for single crystal  
silicon or germanium in making a semiconductor field  
20 effect transistor. There is no recognition of the unique  
properties of these polymers in this patent and, in fact,  
the polymers are treated as semiconducting material even  
though the properties of the polymers are distinctly  
different from that of silicon or germanium. The polymers  
25 are used as substitutes for semiconducting materials

1 sensitive to electrical signals for uses such as in memory  
storage. Disadvantages to the FET as disclosed are that  
it is unstable and has a short useful life.

5 It is therefore an object of the present  
invention to provide a process for producing  
microelectronic devices responsive to chemical input which  
can be incorporated into microelectronic systems which are  
responsive to electrical input.

10 A further object of the present invention is to  
provide a process for constructing molecule-based  
microelectronic devices on silicon substrates which can  
easily be integrated with solid state silicon devices for  
signal processing.

15 Still another object of the invention is to  
provide small, sensitive, and specific microelectronic  
devices with very low power requirements.

20 A further object of the invention is to provide  
diodes, transistors, sensors, surface energy storage  
elements, and light-emitting microelectrode devices which  
can be controlled by molecular-level changes in  
electroactive polymer components.

#### Summary of the Invention

25 The present invention is a process for making  
microelectronic devices which can be controlled by

1       molecular-level changes in electroactive polymer  
components. These devices are fabricated by  
functionalizing electrodes formed by deposition of metal  
on silicon dioxide substrates using convention masking and  
5       photolithography techniques with polymers whose physical  
properties change in response to chemical signals. The  
key features are the small dimension of the electrodes and  
the small spacing, in the range of less than five microns,  
between them.

10               In one embodiment, an analogue of a solid state  
transistor, wherein a transistor is defined as a material  
whose resistance can be adjusted by an electrical signal,  
is formed from an array of gold microelectrodes  
derivatized with a redox polymer such as polypyrrole.  
15       When polypyrrole is oxidized, it conducts an electrical  
current between the microelectrodes. As in a solid state  
transistor, the current between the two outer  
microelectrodes of the array can be varied as a function  
of the potential of the polymer electrically connecting  
20       the electrodes in a manner analagous to the "gate" of a  
transistor. As the potential is altered, the oxidation or  
reduction of the polypyrrole can be effected. This device  
amplifies the very small signal needed to turn the  
polypyrrole from its reduced and insulating state to its  
25       oxidized and conducting state. Further variations are

1 possible using additional polymers with different redox potentials.

5 In a second embodiment, a diode is fabricated on a silicon dioxide-silicon substrate from an array of two or more microelectrodes separated from each other by a distance of 2 microns or less, individually functionalized with a chemically responsive polymer, such as a redox polymer. Examples of redox polymers are polypyrrole, poly-N-methylpyrrole, polythiophene, poly-3-methyl-  
10 thiophene, polyvinylferrocene, derivatized styrene and polyaniline. As many different polymers may be used as there are pairs of microelectrodes. Since the polymers respond at different potentials, each pair of electrodes can be effectively isolated from the other  
15 microelectrodes.

20 In yet another embodiment, a microelectronic device with transistor or "triode-like" properties is fabricated by deposition of polyaniline onto an array of two or more gold microelectrodes. Polyaniline, a redox polymer, has the unusual property of being insulating at an electrical potential, less than +0.1 V vs. SCE in aqueous 0.5 M NaHSO<sub>4</sub>, greater than 10<sup>6</sup> times more  
25 conducting at a slightly higher electrical potential, + 0.4 V vs. SCE in 0.5 M NaHSO<sub>4</sub>, and insulating at a higher electrical potential, +0.7 V vs. SCE in 0.5 M NaHSO<sub>4</sub>. The

1 exact potential at which the polyaniline is conducting or  
insulating is determined by the medium, the amount of  
polyaniline connecting the electrodes, and interactions  
with other polymers. This device is particularly useful  
5 as an electrical switch between a specific range of  
potentials or as a pH or other chemical sensor. The  
device may be further modified for use as an oxygen or  
hydrogen sensor by connecting the polyaniline to a noble  
metal electrode such as a platinum electrode or by  
10 dispersing particles of noble metals such as palladium  
into the polyaniline.

Other specific embodiments of the present  
invention include surface energy storage elements and  
light-emitting microelectrodes.

15

#### Brief Description of the Drawings

Fig. 1 is a cross-sectional view of a surface  
energy storage device wherein electrical energy is used to  
charge the device by reducing a polyviologen polymer,  
20  $(PQ^{2+/+})_n$ , and oxidizing a polyvinylferrocene polymer,  
 $(FeCp_2^{+/0})_n$ .

Fig. 2 is a cross-sectional view of a molecule-  
based transistor consisting of three gold microelectrodes,  
derivatized with polypyrrole and immersed in electrolyte,  
25 with a schematic showing how the electrical potential of



1 the gate is set using a potentiostat with a counter  
electrode and a saturated calomel reference electrode  
(SCE).

5 Fig. 3 is a graph showing the output  
characteristics of the transistor of Fig. 2 as  $I_D$ , the  
current between source and drain, as a function of  $V_D$ , the  
potential between source and drain, at various fixed gate  
potentials,  $V_G$ .

10 Fig. 4a is a cross-sectional view of a molecule-  
based transistor, consisting of two gold electrodes coated  
with polyvinylferrocene,  $(\text{FeCp}_2^{+/0})_n$ , and polyviologen,  
 $(\text{PQ}^{2+/+})_n$ , and functionalized with a quinone-based  
polymer,  $(\text{Q/QH}_2)_n$ , having a pH-dependent redox potential  
which is more negative or positive than the potential of  
15 the viologen polymer, depending on the pH.

Fig. 4b is a schematic of the effect of pH  
variation on the polymers in the transistor of Fig. 4a and  
shows the approximate relationship of the redox  
potentials.

20 Fig. 5 is a cross-sectional view of a molecule-  
based diode consisting of two gold microelectrodes  
derivatized with two polymers of different redox  
potentials.

25 Fig. 6 is a cross-sectional view of an array of  
eight gold microelectrodes derivatized with different  
amounts of polypyrrole.

1                    Fig. 7 is a graph of cyclic voltammograms at 100  
mV/s for an array like that in Fig. 6 in  $\text{CH}_3\text{CN}/0.1\text{M}$   $[\text{n-Bu}_4\text{N}]\text{ClO}_4$ . The bottom portion of the sketch is the  
5                    expected result based on the derivatization procedure and  
electrochemical response.

                  Fig. 8a is a graph of the potential, V vs. SCE,  
measure in  $\text{CH}_3\text{CN}/0.1\text{M}$   $[\text{n-Bu}_4\text{N}]\text{ClO}_4$ , of five gold  
microelectrodes connected with polypyrrole when one is  
under active potential control at  $-1.0$  V vs. SCE and one  
10                    is at a positive potential at which the polypyrrole is  
expected to be conducting.

                  Fig. 8b is a graph of the potential, V vs. SCE,  
of five gold microelectrodes connected with polypyrrole  
where only one electrode is under active potential  
15                    control.

                  Fig. 9 is a graph of the current,  $i$ , measured  
between electrodes, versus applied potential,  $V_{\text{appl}}$  vs.  
SCE, for two adjacent microelectrodes connected with  
polypyrrole as a function of  $V_{\text{set}}$ , where  $V_{\text{set}}$  is the fixed  
20                    potential vs. SCE of one of the two electrodes, and  $V_{\text{appl}}$ ,  
where  $V_{\text{appl}}$  is the potential of the other electrode.

                  Fig. 10 is a graph comparing the diode  
characteristics for two microelectrodes connected with (a)  
polypyrrole and (b) poly-N-methylpyrrole where the fixed  
25                    potential,  $V_{\text{set}}$ , in (a) is  $-1.0$  V vs. SCE and in (b) is  
 $-0.6$  V vs. SCE.

1                    Fig. 11 is a cross-sectional view of a light-  
emitting pair of microelectrodes wherein the two gold  
microelectrodes are connected by a polymer such that  
application of a voltage, approximately 2.6 V, results in  
5                    emission of light characteristic of an excited tris, 2,  
2'-bipyridine ruthenium (II) complex,  $\text{Ru}(\text{bpy})_3^{2+}$ .

                  Fig. 12 (inset) is a cross-sectional view of a  
device fabricated from two polyaniline-coated gold  
microelectrodes wherein  $V_D$  is the potential between one  
10                   microelectrode "source" and another microelectrode "drain"  
at a fixed gate potential,  $V_G$ , controlled relative to an  
aqueous saturated calomel reference electrode (SCE).

                  Fig. 12a is a graph of the drain current,  $I_D$ , in  
microamps versus the drain voltage,  $V_D$ , in mV for the  
15                   device shown in the inset at various values of  $V_G$ , where  
the charge passed in setting the gate to a potential where  
there is conductivity between source and drain can be  
regarded as an input signal.

                  Fig. 12b is a graph of  $I_D$  vs.  $V_G$  at a fixed  $V_D$   
20                   of 0.18 V for the device shown in the inset.

                  Fig. 13 is a graph of a cyclic voltammogram at  
100 mV/s for a device such as the one described in Fig. 12  
(inset) when  $V_G$  is +0.3 V vs. SCE and  $V_D$  is 20 mV. ---- is  
at 0 hours and .... is after 16 hours.

25

1                    Fig. 13 (inset) is a graph of  $I_D$  versus time in hours when  $V_D$  is at 20 mV,  $V_G$  is at +0.3 V vs. SCE, and the electrolyte is 0.5 M  $\text{NaHSO}_4$  at pH 1.

5                    Fig. 14a is a graph of the  $I_D$  vs.  $V_G$  for a device such as the one shown in Fig. 12 (inset), where  $V_G$  is varied from -0.2 V vs. SCE to +0.8 V vs SCE.

                  Fig. 14b is a graph of resistance in ohms versus  $V_G$  for a device such as the one in Fig. 12 (inset).

10                   Fig. 15 is a graph for a device such as the one shown in Fig. 12 (inset) of  $I_D$  in microamps versus  $V_D$  in mV at a  $V_G$  of -0.2 V vs. SCE, a potential at which polyaniline is reduced and insulating.

15                   Fig. 16 is a graph of  $I_D$  versus time in seconds at  $V_D$  of 0.18 V for a device such as the one shown in Fig. 12 (inset) for a  $V_G$  step of -0.2 to +0.3 V vs SCE.

                  Fig. 17 is a cross-sectional view of a polyaniline-connected microelectrode array connected externally to a macroscopic indicator electrode.

20                   Fig. 18 is a cross-sectional view of a polyaniline-connected microelectrode array consisting of three gold microelectrodes connected to a counter-electrode, reference electrode, and potentiostat.

1 Detailed Description of the Invention

          The present invention is a process for producing  
molecule-based microelectronic devices consisting of two  
or more microelectrodes separated by a small dimension,  
5 which can be contacted individually and independently  
functionalized using electroactive polymers with specific  
properties that are responsive to chemical and/or  
electrical signals. Examples of one group of  
electroactive polymers are redox polymers which are  
10 insulating when reduced and conducting when oxidized.

          The microelectrodes are small, typically on the  
order of 2 to 5 microns wide by 50 to 150 microns long by  
0.1 to 0.15 microns thick, although even smaller  
electrodes may be utilized, and made of inert,  
15 electrically conductive material such as gold, silver,  
palladium, gold-platinum, and gold-palladium or other  
metals that are electrochemically inert. The conductor  
should be easily deposited and have low electrical  
resistance, good adhesion to the substrate, stability,  
20 and ability to be functionalized.

          These electrodes are positioned on an inert  
substrate. An example of a preferred substrate would be  
oxidized silicon wafers made by growing a 4500 Angstroms  
to 10,000 Angstroms thick  $\text{SiO}_2$  layer on  $\langle 100 \rangle$  Si. Devices  
25 made according to the present invention on silicon wafers

1 may be easily integrated into presently available solid  
state microelectronic devices, most of which are also  
produced on silicon wafers.

5 The small separation between electrodes,  
typically on the order of 0.1 to 2 microns, combined with  
the use of electroactive polymers with specific  
properties, is crucial to the invention. The smallest  
inter-electrode space technically feasible is preferred.  
10 The small inter-electrode space allows high current  
densities. As the distance between microelectrodes is  
increased, output decreases and "noise" increases. The  
direction of current flow, the ability to respond to a  
chemical signal such as a change in pH, the rate of  
response, the degree of response, the storage of energy,  
15 and the ability to place other pairs of electrodes in  
close proximity without interference is due to the choice,  
deposition, degree of separation and quantity of polymer.

Various groups of polymers known to those  
skilled in the art are suitable for use in the present  
20 invention. The requirements for such polymers are that  
they can be electrochemically deposited on individual  
electrodes and polymerized and that they can respond to a  
signal, in a reversible manner, in a way which can be  
electrochemically detected. Such materials are described  
25 by R.W. Murray in Electroanalytical Chemistry, Vol. 13,  
Edited by A.J. Bard (Marcel Dekker, N.Y., 1984).

1            Suitable electrochemically polymerizable  
materials for use in the present invention include redox  
polymers. Examples of such polymers are polypyrrole,  
polyaniline, poly-N-methylpyrrole, polythiophene, poly-3-  
5 methylthiophene and polyvinylferrocene (poly vinyl  
dicyclopentadienyliron). Styrene and vinyl aromatic  
derivatives such as vinyl pyridine, vinyl,2,2'-bipyridine  
and metal complexes of these derivatives, are also useful  
since they can be electrochemically polymerized and may be  
10 derivatized with a number of reagents, including  
biologically active agents such as enzymes and ionophores  
that complex with ions such as lithium and calcium.

          Using two or more electrodes connected with one  
polymer, a transistor-like device may be fabricated. By  
15 choosing two or more polymers with different redox  
potentials, adjacent electrodes may be electronically  
isolated or made to function as diodes or surface energy  
storage units.

          For polypyrrole and poly-N-methylpyrrole, the  
20 oxidized materials are electronic conductors. The  
conductivity varies by more than  $10^{10}$  depending on the  
redox state of the polymers. The consequence of the very  
large difference in conductivity with redox state is that  
the potential drop can occur across a very small fraction  
25 of length of the connecting polymer when one

1 microelectrode is held at a potential where the polymer is  
reduced and insulating and the other is held at a  
potential where the polymer is oxidized and conducting.  
For example, polypyrrole is insulating at approximately  
5 -0.4 V vs. SCE potential but becomes conducting at  
positive potentials up to any positive potential at which  
the polypyrrole is durable. The actual conductivities of  
the oxidized polymers, measured in  $\text{CH}_3\text{CH}/0.1 \text{ M } [\text{n-}$   
 $\text{Bu}_4\text{N}]\text{ClO}_4$ , of polypyrrole and poly-N-methylpyrrole,  
10 respectively, are approximately  $10^{-2} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$  and  $10^{-4}$   
to  $10^{-5} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$ .

In contrast to polypyrrole, polyaniline can be  
made conducting by either a positive or a negative shift  
of the electrochemical potential, since polyaniline is  
15 essentially insulating at sufficiently negative (negative  
of 0.0 V vs. SCE) or positive (positive of +0.7 V vs. SCE)  
electrochemical potentials. As a result, a polyaniline-  
based device responds to a signal in a significantly  
different way from solid state transistors where the  
20 current passing between source and drain,  $I_D$ , at a given  
source to drain voltage,  $V_D$ , does not decrease with  
increasing gate voltage,  $V_G$ . The conductivity of  
polyaniline has been measured to span eight orders of  
magnitude and is sensitive to pH and other chemical  
25 parameters.



1           The potential at which a polymer exhibits a  
sharp change in conductivity due to oxidation is the  
threshold potential,  $V_T$ .  $V_T$  can be manipulated by using  
different monomers or different redox polymers, and by  
5           varying the medium to be "seen" by the polymer.

Other polymers which are useful in the present  
invention include redox polymers known to be  
electrochromic materials, compounds which change color as  
a result of electrochemical reactions. Examples of such  
10           materials are polyvinylferrocene, polynitrostyrene and  
viologens. Viologens, described by Wrighton et al. in  
U.S. Patent Nos. 4,473,695 and 4,439,302, are compounds  
formed from 4,4'-bipyridinium which may be polymerized and  
covalently bonded or otherwise confined to the surfaces of  
15           electrodes. Viologens such as dialkyl-4,4'-bipyridinium  
di-cation and associated anions, dichloride, dibromide, or  
di-iodide, form contrasting colors when oxidized or  
reduced. Since each monomer unit of viologen has a 2+  
charge which is balanced in the presence of two halide  
20           counter ions, the counter ions can be replaced with a  
complex ion such as  $PtCl_6^{2-}$  which can then be reduced to  
yield embedded elemental Pt(0) in highly dispersed form.  
An enzyme such as hydrogenase can also be immobilized onto  
or throughout the redox polymer to equilibrate the redox  
25           polymer with the enzyme substrates.

1                   Substituted viologens are useful for  
photogeneration of hydrogen from aqueous electrolytes, for  
reduction of metal-containing macromolecules, and on p-  
type silicon photocathodes in electrolytic cells.

5                   The invention is further illustrated by the  
following non-limiting examples. Devices in these  
examples were constructed according to the procedure  
outlined below, with minor variations.

10           Fabrication of Microelectrode Arrays

                  Microelectrode arrays were fabricated in the  
Massachusetts Institute of Technology Microelectronics  
Laboratory in the Center for Materials Science and  
Engineering which includes a class 100 clean room and is  
15           equipped to meet the specialized requirements for the  
production of solid state microelectronic devices such as  
"silicon chips".

                  A two-mask process was designed. The first mask  
was made for a metal lift-off procedure to form  
20           microelectrodes, leads, and contact pads. The second mask  
was made to pattern a photoresist overlayer leaving a 50  
to 140 micron length of the microelectrodes and the contact  
pads exposed.

                  A microelectrode array was designed using the  
25           Computer Aided Design Program HPEDIT at a Hewlett Packard

1 Model 2648A graphics terminal on a DEC-20. The design  
file was translated into Caltech Intermediate Form  
(CIF). This CIF file was translated to Mann compatible  
code and written on magnetic tape. Masks for  
5 photolithography were made from the file on magnetic tape  
using a Gyrex Model 1005A Pattern Generator. E-K 5" X 5"  
X 0.090" Extra Flat high resolution glass emulsion plates  
were used to make the photolithography masks. The  
emulsion plates were developed by a dark field process.

10 p-Si wafers of 100 orientation, two inches in  
diameter and 0.011 inches thick, obtained from Wacker  
Corp. were used as substrates upon which to fabricate the  
microelectrode arrays. The silicon wafers were RCA  
cleaned in a laminar air flow hood in the class 100 clean  
15 room. The wafers were immersed in hot aqueous 6% by  
volume  $H_2O_2$ /14% by volume aqueous  $NH_3$ , briefly etched in  
hydrofluoric acid diluted 10:1 with deionized water,  
immersed in hot aqueous 6% by volume  $H_2O_2$ /14% by volume  
HCl, rinsed in deionized water (resistance greater than 14  
20 Mohm cm), and spun dry. The cleaned wafers were loaded  
immediately into an oxidation tube furnace at 1100°C under  
 $N_2$ . For examples 1 to 5, a dry/wet/dry/anneal oxidation  
cycle was used to grow a thermal oxide layer 4500  
Angstroms thick. For example 6, a dry oxidation cycle was  
25 used to grow a thermal oxide 11850 Angstroms thick. Oxide

1 thicknesses were measured using a Gaertner Model L117  
ellipsometer. The oxidized wafers were taken immediately  
to the photolithography stage.

5 Each oxidized wafer was flood-coated with  
hexamethyl-disilazane and spun at 6000 rpm for 20 sec.  
For examples 1 to 5, one ml of MacDermid Ultramac PR-914  
positive photoresist was syringed onto each wafer. The  
wafer coated with resist was spun for 30 sec at 4000 rpm  
and then prebaked 35 min at 90°C. For example 6, one ml of  
10 Shipley 1470 positive photoresist was syringed onto each  
wafer and the wafer spun for 30 seconds at 6000 rpm. The  
coated wafer was then prebaked 25 minutes at 90°C.

A GCA Mann 4800 DSW Wafer Stepper was used to  
expose the photoresist. The Mann uses the 405 nm line of a  
15 350 W Hg arc lamp as a light source. The mask image is  
reduced 5:1 in the projection printing. For examples 1 to  
5, an exposure time of 0.850 sec was used and the  
photoresist developed 60 sec in MacDermid Ultramac MF-62  
diluted 1:1 with deionized water. For example 6, the wafer  
20 was exposed for 1.2 seconds and developed 60 seconds in  
Shipley 312 developer diluted 1:1 with dionized water.  
The developed wafers were then cleaned in a planar oxygen  
etching chamber at 75-100 W forward power in 20 mtorr of  
oxygen for 15 seconds.

1                   A bilayer metallization was performed. A MRC  
8620 Sputtering System was used in preparing the  
microelectrode arrays of examples 1 to 5. The bilayer  
metallization of the wafers used in example 6 was  
5 performed in a NRC 3117 electron beam evaporation  
system. Wafers were placed on a quartz plate that was  
freshly coated with chromium. The wafers were  
backspattered 2 min at 50 W forward power in an argon  
plasma at 5 mtorr. Chromium was sputtered at 50 W forward  
10 power to produce a layer of chromium. The layer on the  
wafers in examples 1 to 5 was 200 Angstroms thick. The  
layer in example 6 was 50 Angstroms thick. Gold was then  
sputtered at 50 W forward power to produce a layer 1000  
Angstroms thick. Chromium serves as an adhesion layer for  
15 the gold. The combined chromium/gold thickness of the  
wafers used in example 6 was measured to be 1052 Angstroms  
on a Dektak II surface profile measuring device.

At this point, the chromium/gold was in direct  
contact with the  $\text{SiO}_2$  substrate only in the areas that  
20 were to form the microelectrodes, leads, and contact pads  
and on photoresist in all other areas. The chromium/gold  
on photoresist was removed by a lift-off procedure: the  
metallized wafers were immersed in warm acetone, in which  
soft-baked positive photoresist is soluble, for 75 minutes  
25 for the wafers used in examples 1 to 5 and 5 minutes for

1 the wafers used in example 6. The wafers used in examples  
2 1 to 5 were briefly sonicated in acetone to remove the  
3 metal between microelectrodes, dried, and then cleaned of  
4 residual photoresist in a planar oxygen plasma etching  
5 chamber at 200 W forward power in 50 mtorr oxygen for 60  
6 sec.

7 The wafers used in example 6 was blasted with  
8 acetone from a Paasche air brush with N<sub>2</sub> at 70 psi,  
9 sonicated for 30 minutes in acetone, then rinsed with  
10 acetone and methanol before drying. The wafers were then  
11 cleaned in a mixture of hot aqueous 6% by volume H<sub>2</sub>O<sub>2</sub>/14%  
12 by volume aqueous NH<sub>3</sub>, rinsed in deionized water (greater  
13 than 14 megaohm-cm), and spun dry. The wafers were then  
14 baked at 180°C for 40 minutes before repeating the  
15 photoresist spin coating process. The wafers were again  
16 prebaked at 90°C for 25 minutes and then exposed in a Karl  
17 Suss Amercia Inc. Model 505 aligner for 11 seconds, using  
18 a dark field mask. The photoresist was developed in  
19 Shipley 312 developer diluted 1:1 with deionized water to  
20 expose the bond pads and the array of microelectrode  
21 wires. The exposed areas were cleaned of residual  
22 photoresist in the oxygen plasma etching chamber at 75-100  
23 W for 1 minute. The remaining photoresist was hardbaked  
24 at 180°C for 15 hours.

1                   Wafers were then baked at 180°C for 40 minutes  
before repeating the photoresist spin coating process.  
The wafers were again prebaked at 90°C for 25 minutes and  
then exposed in a Karl Suss American Inc. Model 505  
5                   aligner for 11 seconds, using a dark field mask. The  
photoresist was developed to Shipley 312 developer diluted  
1:1 with deionized water to expose the bond pads and the  
array of microelectrode wires. The exposed areas were  
cleaned of residual photoresist in the oxygen plasma  
10                  etching chamber at 75-100 W for 1 minute. The remaining  
photoresist was hard baked at 180°C for 15 hours.

                  Individual die (chips) were scribed and  
separated. The chips were mounted on TO-5 headers from  
Texas Instruments with Epoxi-Patch 0151 Clear from Hysol  
15                  Corp. A Mech-El Ind. Model NU-827 Au ball ultrasonic  
wire bonder was used to make wire bonds from the chip to  
the TO-5 header. The leads, bonding pads, wire bonds, and  
header were encapsulated with Epoxi-Patch\*0151. The  
header was connected through a TO-5 socket to external  
20                  wires. The external wires were encased in a glass tube.  
The header was sealed at the distal end of the glass tube  
with heat shrink tubing and Epoxi-Patch 1C white epoxy  
from Hysol Corp.

                  Prior to use as a microelectrode array, the  
25                  array was tested to establish the leakage current between

\* Trade mark

1 the various electrodes of the array. Arrays characterized  
as usable have a measured resistance between any two  
electrodes of greater than  $10^9$  ohms in non-aqueous  
electrolyte solution containing no added electroactive  
5 species. In many cases only a fraction of the electrodes  
of an array were usable. Prior to use in experimentation  
the microelectrode arrays were tested further in aqueous  
electrolyte solution containing 0.01M  $K_3[Fe(CN)_6]$  and 0.01  
M  $K_4[Fe(CN)_6]$  or with  $[Ru(NH_3)_6]Cl_3$  to establish that the  
10 microelectrodes give the expected response. Typically, a  
negative potential excursion to evolve  $H_2$  cleaned the gold  
surface sufficiently to give good electrochemical response  
to the  $Fe(CN)_6^{3-/4-}$  or  $Ru(NH_3)_6^{3+/2+}$  redox couples. The  
electrolyte used for electrical measurement was 0.1 M  
15  $NaClO_4$  in  $H_2O$  solvent, 0.5 M  $NaHSO_4$ , or 0.1 M  $[n-Bu_4N]ClO_4$   
in  $CH_3CN$  solvent.

#### Electrochemical Equipment

Most of the electrochemical experimentation in  
20 examples 1 to 5 was carried out using a Pine Model RDE 3  
bipotentiostat and potential programmer. In cases where  
two microelectrodes were under active potential control  
and a third was to be probed, a PAR Model 363  
potentiostat/galvanostat was used in conjunction with the  
25 Pine Model RDE 3. All potentials were controlled relative



1 to an aqueous saturated calomel reference electrode  
(SCE). Typically, electrochemical measurements were  
carried out under N<sub>2</sub> or Ar at 25°C.

For example 6, most of the electrochemical  
5 experimentation was carried out using a Pine Model RDE 4  
bipotentiostat and potential programmer. In some cases  
where only a single potentiostat was needed a PAR Model  
173 potentiostat/galvanostat and a PAR Model 175 universal  
programmer was used. Potential step experiments were  
10 carried out using the RDE 4 with a Tektronix type 564B  
storage oscilloscope as the recorder.

#### Derivatization of Microelectrodes

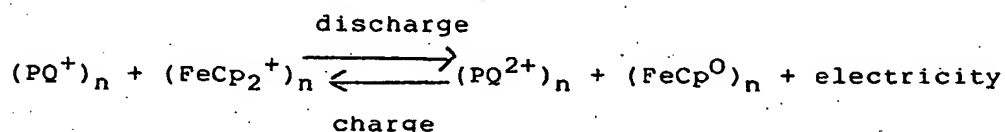
In examples 1 to 5, the gold microelectrodes  
15 were functionalized by oxidation of 25-50 mM pyrrole or N-  
methylpyrrole in CH<sub>3</sub>CN/0.1 M [n-Bu<sub>4</sub>N]ClO<sub>4</sub>. The  
polypyrrole was deposited at +0.8 V vs. SCE, and the poly-  
N-methylpyrrole was deposited at +1.2 vs. SCE. The  
deposition of the polymer can be effected in a controlled  
20 manner by removing the array from the derivatization  
solution after passing a certain amount of charge.  
Electrodes were then examined by cyclic voltammetry in  
CH<sub>3</sub>CN/0.1 M [n-Bu<sub>4</sub>N]ClO<sub>4</sub> to assess the coverage of polymer  
and to determine whether the polymer coated two or more  
25 electrodes resulting in a "connection" between them.

1 Prior to use as a microelectrode array, each  
microelectrode wire in the devices used in example 6 was  
tested with an ohmmeter to make sure it was not shorted to  
any other wire on the device. Then each microelectrode  
5 was tested by running a cyclic voltammogram in 0.01 M  
 $\text{Ru}(\text{NH}_3)_6^{3+}$ /0.1 M  $\text{NaNO}_3/\text{H}_2\text{O}$ . The microelectrodes were  
derivatized by oxidation of a stirred 0.44 M aniline  
solution in 0.5 M  $\text{NaHSO}_4/\text{H}_2\text{O}$  at pH 1. The polyaniline was  
deposited at +0.9 V vs. SCE. Electrodes were then  
10 examined by cyclic voltammetry in 0.5 M  $\text{NaHSO}_4$  at pH 1 to  
assess the coverage of polymer and to determine whether  
the polymer coated two or more electrodes resulting in a  
connection between them. Macroscopic gold electrodes were  
derivatized with polyaniline by the same procedure to  
15 accurately relate the thickness of polyaniline to cyclic  
voltammetry response and the charge passed in the anodic  
deposition. Typically, a portion of the gold flag was  
covered with grease prior to depositing the polyaniline  
over the exposed gold surface. The grease was then  
20 removed with  $\text{CH}_2\text{Cl}_2$  to give a well defined step from gold  
to polyaniline.

#### Example 1

25 In one embodiment of the present invention,  
depicted in Fig. 1, a surface energy storage device 10 is

constructed from two gold microelectrodes 12, 3 microns wide by 140 microns long by 0.12 microns thick, deposited on a 1 micron thick SiO<sub>2</sub> insulator 14 grown on a 100 Si substrate 16 and separated by a distance of 1.4 microns. Each microelectrode is individually coated with electrochemically deposited and polymerized polymers, polyviologen 18 and polyvinylferrocene 20. Electrical energy can be used to charge the device by reducing the polyviologen, the (PQ<sup>2+</sup>)<sub>n</sub> polymer, and oxidizing the polyvinylferrocene, the (FeCp<sub>2</sub><sup>0</sup>)<sub>n</sub> polymer, according to the following reaction:



#### Example 2

In another embodiment of the present invention, shown in Fig. 2, a molecule-based transistor 22 is fabricated from three gold microelectrodes separated by 1.4 microns, derivatized with polypyrrole 24. Typical coverage of the polypyrrole is 10<sup>-7</sup> mol/cm<sup>2</sup> of exposed gold, and the individual microelectrodes are electrically connected. The microelectrodes are wired so as to correspond to the drain 26, gate 28, and source 30 as in a conventional solid state transistor.

1           The properties of the device are characterized  
by immersing the device in an electrolyte,  $\text{CH}_3\text{CN}/0.1\text{M}$  [ $n\text{-Bu}_4\text{N}]\text{ClO}_4$ , and measuring the current 32 between source 30  
5           and drain 26,  $I_D$ , as a function of the potential 34  
between source and drain,  $V_D$ , at various fixed gate  
potential 36,  $V_G$ . The results are shown in Fig. 3.

          At values for  $V_D$  of less than 0.5 V, the device  
is "off" when  $V_G$  is held at a negative potential where the  
polypyrrole is expected to be insulating and  $I_D$  is  
10          small. When  $V_G$  is moved to potentials more positive than  
the oxidation potential of polypyrrole, approximately -0.2  
V vs. SCE, the device "turns on" and a significant steady-  
state value for  $I_D$  can be observed for modest values of  
 $V_D$ . The close spacing of the microelectrodes allows an  
15          easily measurable current to pass between the source 30  
and the drain 26 when  $V_D$  is significant and  $V_G$  is above  
the threshold,  $V_T$ .  $V_T$ , the gate potential at which the  
device starts to turn on, is approximately equal to the  
redox potential of polypyrrole. For  $V_G$  more positive than  
20           $V_T$ , the value of  $I_D$  increases at a given value of  $V_D$ , in a  
manner consistent with the increasing conductivity due to  
an increasing degree of oxidation. At sufficiently  
positive values of  $V_G$ , greater than or equal to +0.5 V vs.  
SCE,  $I_D$  becomes insensitive to further positive movement  
25          of  $V_G$  at a given value of  $V_D$ , a result consistent with

1 measurements of the resistance of the oxidized polypyrrole  
coated on a microelectrode array. A small range of  $V_D$   
values (0 to 0.2 V) is used to minimize electrochemical  
reactions at the source 30/polymer 24 and drain 26/polymer  
5 24 interfaces.

A fraction of  $10^{-8}C$  of charge is required to  
obtain the maximum steady-state value of  $I_D$  when  $V_D$  is  
equal to 0.2 V with this device. The value of  $I_D$   
achievable with the device is  $4 \times 10^{-5}C/s$ . It is apparent  
10 from these results that a small signal to the gate  
microelectrode can be amplified in much the same way that  
a small electrical signal can be amplified with a solid  
state transistor. The major difference is that the turn  
on/turn off time in the molecule-based system is dependent  
15 on the rate of a chemical reaction rather than on electron  
transist times across the souce to drain distance. For  
the molecule-based system, the properties such as  $V_T$  and  
minimum turn on signal can be adjusted with rational  
variation in the monomer used to prepare the polymer. Use  
20 of smaller dimensions and materials other than polypyrrole  
can also lead to faster switching times.

### Example 3

As shown in Fig. 4a, a molecule-based pH sensor  
25 40 can theoretically be fabricated using a two  
microelectrode array on a  $SiO_2$ -Si substrate 42.

1           The two gold microelectrodes 44, 45 are coated  
with polyviologen 46,  $(PQ^{2+}/^+)_n$ , and polyvinylferrocene  
48,  $(FeCp_2^{+/0})_n$ , respectively, and then overlaid with  
5           another polymer 50 with a different pH dependent redox  
potential, such as a polyquinone,  $(Q/QH_2)_n$ , whose redox  
potential is above the redox potential of the polyviologen  
at high pH and between that of the polyviologen and  
polyvinylferrocene at low pH.

10           The pH variation serves as the signal to be  
amplified. Varying the pH results in a variation in  
current passing between the two gold electrodes at a fixed  
potential difference with the negative lead to the  
viologen coated electrode. As shown by Fig. 4b,  
alteration of the pH changes the redox potential of  
15           polymer 50. Low pH acts to make it easier to reduce  
polymer 50. Current can flow between source 44 and drain  
45 when the negative lead is attached to the polyviologen-  
coated gold microelectrode 44 and the positive lead is  
connected to the polyvinylferrocene-coated gold  
20           microelectrode 45 and the redox potential of the  
polyquinone is between the redox potentials of the two  
polymers 46 and 50 coating source 44 and drain 45. At a  
fixed potential difference, the current passing between  
the two microelectrodes 44 and 45 should depend on the pH  
25           of the solution contacting the polymer 50.

1           A pH sensor may also be fabricated by coating a  
microelectrode array with a polymer such as polyaniline.  
For a device consisting of two gold microelectrodes, 0.1  
micron thick, 4.4 microns wide, and 50 microns long,  
5           separated by a distance of 1.7 microns, coated with a  
layer of polyaniline approximately 5 microns thick,  
changes in the pH of the surrounding medium markedly alter  
the conductivity. For example, the value of  $I_D$  at  $V_D$   
equal to 20 mV and  $V_G$  of 0.2 V vs. SCE is reduced upon  
10          raising the pH of the solution, where  $I_D$  is the current  
between one electrode and the next,  $V_D$  is the potential  
between the first and second electrode, and  $V_G$  is the  
potential between the two electrodes and a saturated  
calomel reference electrode.  $I_D$  at pH 1 is approximately  
15           $10^2$  times greater than at pH 6.

          Polyaniline is limited to use with solutions of  
pH less than 6 to preclude irreversible chemical changes  
that occur at the higher pH values. However, other pH-  
sensitive redox polymers may be used to fabricate  
20          microelectrode pH-sensors for other pH ranges.

          Numerous uses in chemical systems are possible  
for such sensing devices. For example, such a device may  
be used to detect subtle changes in pH of aqueous  
solutions. Electrical signals generated by the device  
25          could be directly amplified and processed further.

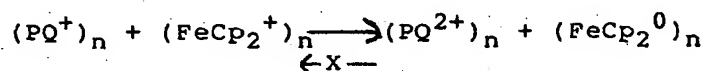
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Example 4

A molecule-based diode 50, produced according to the present invention, is shown in Fig. 5.

Microelectrodes 52 and 54 are each individually covered  
 5 with polymers 56 and 58 having very different redox potentials. The current passes between the two heavily coated, connected microelectrodes 52 and 54 as a function of the threshold potential of the diode, which is dependent on the redox potentials of the polymers.  
 10 Electrons only flow from microelectrode 52 to microelectrode 54 due to the large difference in the redox potentials of the two polymers 56 and 58. For example, for a polyviologen/-polyvinylferrocene diode, charge will pass only when the negative lead of the applied potential is connected to the gold electrode 52 coated with  
 15 polyviologen 56 and the positive lead is attached to the gold electrode 54 coated with polyvinylferrocene 58. This reaction is shown as:

20



As shown in Fig. 6, it is possible to electrochemically deposit electroactive polymers 60 on individual electrodes 62a-h in variable amounts. The electrodes 62e-

25



1 n which are bridged by the polymer 60 are electrically  
connected: charge can pass from one microelectrode 62e to  
another microelectrode 62f-h via conduction mechanisms of  
the polymer 60. Connected electrodes are typically  
5 associated with coverages of approximately  $10^{-7}$  mol  
polymer/cm<sup>2</sup> electrode. Addressing one electrode oxidizes  
and reduces the polymer 60 over all of the electrodes  
62e-h.

Fig. 7 shows the cyclic voltammetry of the  
10 polypyrrole modified array of Fig. 6 in CH<sub>3</sub>CN/0.1M [n-  
Bu<sub>4</sub>]ClO<sub>4</sub> containing no added redox active species. The  
unfunctionalized electrodes 62a, 62b, and the electrode  
62c, with a negligible amount of polypyrrole, lack the  
cyclic voltammetry signal characteristic of an electrode-  
15 confined polymer. Immediately adjacent to the non-  
derivatized electrodes 62a-c are electrodes 62d-h that  
show cyclic voltammograms characteristic of electrode-  
confined polypyrrole. The shape of the voltammogram is  
nearly the same as for a macroscopic gold electrode  
20 derivatized in the same manner. In addition, the  
potential of the oxidation and reduction peaks are as  
expected for the oxidation and reduction of polypyrrole.

Based on the integration of the charge passed  
upon cycling the derivatized microelectrodes 62  
25 individually between the negative and positive limits, it

1 can be seen that controlled amounts of polypyrrole 60 can  
be deposited on the electrodes 62. The same results, with  
the expected differences in the oxidation and reduction  
potentials, were shown using poly-N-methylpyrrole instead  
5 of polypyrrole.

Figs. 8a and 8b show the spatial potential  
distributions across a polypyrrole array 70 where one  
(Fig. 8b) or two (Fig. 8a) of the electrodes is under  
active potential control. The entire array 70 was  
10 immersed in  $\text{CH}_3\text{CN}/0.1\text{M } [\text{n-Bu}_4]\text{ClO}_4$  and a biopotentiostat  
used to actively control the potential of one (Fig. 8b) or  
two (Fig. 8a) microelectrodes against a common reference  
and counter electrode in the electrolyte solution.

The potential of one microelectrode 72 in the  
15 five electrode array 70 was set at a negative potential of  
-1.0 V vs. SCE and the potential of another microelectrode  
74 varied between 0.0 and 1.0 V vs. SCE.

As shown in Fig. 8a, the potentials of  
electrodes 76, 78, and 80 not under active potential  
20 control are nearly equal to the positive potential applied  
to electrode 74. Although a small potential drop of  
approximately 50 mV occurs over the 9 micron distance  
separating electrodes 74 and 80, the essential finding is  
that nearly all, up to 1.8 V, of the potential drop occurs  
25 across a narrow region immediately adjacent to electrode

1 72 under active potential control at -1.0 V vs. SCE. The  
result is consistent with the difference in conductivity  
between the reduced and oxidized state of the polypyrrole,  
of which the consequence is that the potential drop occurs  
5 across a very small fraction of length of the connecting  
polymer when one microelectrode is held at a potential  
where the polymer is reduced and insulating and another is  
held at a potential where the polymer is oxidized and  
conducting. This would not be an expected result for a  
10 polymer with only a moderate conductivity, such as those  
that exhibit redox conductivity where a linear change in  
concentration of redox centers across the thickness  
spanned by two electrodes at differing potentials would  
give a potential profile predicted by the Nernst equation.

15 Fig. 8b shows that when only one of the  
microelectrodes is under active potential control in the  
positive region, all of the electrodes are at the same  
potential as would be expected when there is an electrical  
connection between them. When one of the microelectrodes  
20 is driven to a negative potential, it would be expected  
that all would ultimately follow. Upon reduction,  
however, the polymer becomes insulating and the rate of  
potential following can be expected to be slower.

25 As shown by the current vs. potential data in  
Fig. 9, polypyrrole connected-microelectrodes behave in

1 a diode-like fashion. Current vs.  $V_{\text{applied}}$  curves are  
shown as a function of the potential,  $V_{\text{set}}$ , at which one  
92 of the electrodes is fixed relative to the SCE. The  
current measured is that passing between the two  
5 microelectrodes. The magnitude of the current passing  
through the other microelectrode is identical to that  
passing through the other microelectrode but opposite in  
sign.

When  $V_{\text{set}}$  is sufficiently positive, the current  
10 vs.  $V_{\text{applied}}$  curve is linear over a wide range of  
 $V_{\text{applied}}$ . The resistance of polypyrrole from the slope of  
such plots is about  $10^3 \text{ ohms}$ . Current densities exceeding  
1  $\text{KA/cm}^2$  were observed. When  $V_{\text{set}}$  is sufficiently  
negative, there is a broad range of the current vs.  
15  $V_{\text{applied}}$  curve where there is insignificant current.  
Therefore, as shown in Fig. 10a, a good diode  
characteristic can be obtained using polypyrrole coated,  
closely spaced microelectrodes. The onset of current  
closely corresponds to the situation where the  $V_{\text{appl}}$ .  
20 results in the conversion of the polypyrrole from its  
reduced and insulating state to its oxidized and strongly  
conducting state.

As shown in Fig. 10b, results using poly-N-  
methypyrrole in place of of polypyrrole in the array  
25 shown in Fig. 9 were similar except that the value of  $V_{\text{set}}$

1 necessary to obtain a current that is linear as  $V_{\text{applied}}$   
is varied is more positive than with polypyrrole. The  
resistance of the poly-N-methylpyrrole is  $10^5$  to  $10^6$   
ohms. Both the higher resistance and the more positive  
5 potential necessary to obtain the conducting regime are  
consistent with the known differences between polypyrrole  
and poly-N-methylpyrrole.

Example 5

10 A light emitting device 98 may also be made  
according to the process of the present invention. As  
shown in Fig. 11, light is emitted from a polymer 100  
overlying two gold microelectrodes 102 on a silicon  
dioxide-silicon substrate 104 when an electrical current  
15 is applied. In the depicted device, light characteristic  
of an excited  $\text{Ru}(\text{bpy})_3^{2+}$  species is emitted when a voltage  
of approximately 2.6 V is applied.

Polymers useful in a light emitting device  
according to the present invention can be polymerized from  
20 any monomers which are electrochemiluminescent, such as  
vinyl derivatives of rubrene or diphenyl anthracene.

Example 6

A triode-like device was also constructed by  
25 electrochemical deposition and oxidation of a polyaniline

1 film onto a microelectrode array consisting of eight gold  
electrodes, 0.1 micron thick, 4.4 microns wide, and 50  
microns long, each individually addressable and separated  
from each other by 1.7 microns.

5 The magnitude of the current passing between  
electrically connected microelectrodes at a given applied  
potential depends on the electrochemical potential of the  
polyaniline. In an electrolyte of aqueous 0.5 M NaHSO<sub>4</sub>,  
the current at a fixed applied potential is maximum at an  
10 electrochemical potential of +0.4 V vs. SCE and declines  
by a factor of greater than 10<sup>6</sup> upon reduction to a  
potential of + 0.1 V vs. SCE or oxidation to + 0.7 V vs.  
SCE.

The polyaniline-functionalized microelectrodes  
15 were examined by cyclic voltammetry in 0.5 M NaHSO<sub>4</sub> at pH  
1 to assess coverage of the polymer and to determine  
whether the polymer coating two or more electrodes results  
in an electrical connection between them. Derivatization  
of the electrode can be controlled by adjusting the amount  
20 of polyaniline by varying the amount of charge passed in  
the electrochemical polymerization. At one extreme, the  
amount of polyaniline can be small enough to derivatize the  
individual microelectrodes but not to electrically connect  
them. At the other extreme, polyaniline can be deposited  
25 in amounts sufficient to electrically connect all of the  
microelectrodes.

1 Both a separate, unconnected microelectrode and  
multiple, connected electrodes show the same cyclic  
voltammogram at 50 mV/s in 0.5 M NaHSO<sub>4</sub> as does a single  
unconnected reference microelectrode at 50 mV/s in 0.5 M  
5 NaHSO<sub>4</sub>. This is consistent with one electrode being  
capable of oxidizing all of the polyaniline present on a  
single microelectrode or on multiple connected micro-  
electrodes. When adjacent derivatized microelectrodes are  
not connected, the sum of the areas under the cyclic  
10 voltammograms for the individual electrodes is the area  
found when the microelectrodes are externally connected  
together and driven as a single electrode. The thickness  
of polyaniline is not measured to be directly proportional  
to the integrated cyclic voltammetry wave as it is for  
15 surface-confined, viologen derived polymers. This lack of  
direct proportionality may be attributable to  
morphological changes in the polymer with increasing  
thickness.

As shown in Fig. 12 (inset), a triode-like  
20 device 110 was constructed by coating two adjacent gold  
microelectrodes 112, 114 with a five to 10 micron thick  
electrochemically deposited and polymerized film of  
polyaniline 116. Measurements were made by immersing the  
device 110 in aqueous 0.5 M NaHSO<sub>4</sub> at 25°C under an inert  
25 atmosphere of N<sub>2</sub> or Ar. Devices constructed in this  
manner exhibit fairly long term stability.

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1           As shown by the cyclic voltammogram in Fig. 13  
for the device 110, the connected pair of electrodes  
exhibits a nearly constant steady state current between  
the two microelectrodes for at least 16 hours when  $V_D$  is  
5   20 mV and  $V_G$  is 0.3 V vs. SCE. In general, devices can be  
used for characterization for several days without  
significant deterioration.

          The conductivity of polyaniline which is  
immersed in an electrolyte such as aqueous 0.5 M  $\text{NaHSO}_4$   
10 depends on the electrochemical potential, which can be  
varied by varying  $V_G$ . As shown in Figs. 14a and 14b, the  
resistance of polyaniline depends on its electrochemical  
potential. The minimum resistance is at an electro-  
chemical potential in the vicinity of +0.4 V vs. SCE.  
15 Changes in resistance in excess of  $10^6$  are routinely  
measured.

          The minimum resistance for polyaniline is  
similar to that for polypyrrole connecting two  
microelectrodes spaced 1.4 microns apart, as shown in  
20 example 3. It is significantly different from  
polypyrrole, however, in that polyaniline is less  
conducting at potentials less than or greater than +0.4 V  
vs. SCE. The change in resistance of polyaniline is  
essentially reversible for potentials less than +0.6 V vs.  
25 SCE. Potentials significantly more positive than +0.6 V



1 vs. SCE yield an increase in the resistance of the  
 polyaniline when the potential is again decreased to +0.4  
 V vs. SCE. The limit of positive applied potential is  
 determined by O<sub>2</sub> evolution and limited durability of the  
 5 polyaniline. The limit of negative applied potential is  
 determined by the onset of H<sub>2</sub> evolution.

As shown in Figs. 12a and 12b, the triode-like  
 device 110 shows an increase and then a decrease in I<sub>D</sub> as  
 V<sub>G</sub> is varied from negative to positive potentials, unlike  
 10 conventional solid state devices which show an increase in  
 I<sub>D</sub> as V<sub>G</sub> is varied until the I<sub>D</sub> ultimately levels off at a  
 constant, V<sub>G</sub>-independent value. The charge passed in  
 setting the gate to a potential where there is  
 conductivity between the source 114 and drain 112 can be  
 15 regarded as an input signal. For the device 110, the  
 charge necessary to completely turn on the device is  
 approximately 10<sup>-6</sup>C.

Transconductance, g<sub>m</sub>, is determined by the  
 equation:

$$\frac{\partial I_D}{\partial V_G} \bigg|_{V_D} = g_m$$

20 Using the data in Figs. 12a and 12b, the maximum  
 value of g<sub>m</sub> for device 110 is approximately 20  
 millisiemens per millimeter of gate width, as determined  
 25 from the rising part of the I<sub>D</sub> - V<sub>G</sub> curve as V<sub>G</sub> is moved  
 to a potential more positive than approximately 0.1 m/V.

1 By convention, gate length in Si/SiO<sub>2</sub>/metal  
field effect transistors (MOSFET) is the separation of  
source and drain. "Width" therefore corresponds to the  
long dimension of the device 110. Since the  $g_m$  of device  
5 110 is only about one-order of magnitude less than that  
for good MOSFET devices, the signal from the polyaniline-  
based device can be fed to conventional MOSFET in the form  
of voltage across a load resistance for further  
amplification.

10 Diode-like behaviour can be obtained using  
device 110, as shown in Fig. 15, at  $V_G$  values where the  
polyaniline is reduced and insulating. Current passes  
between the microelectrodes 112 and 114 when the "source"  
microelectrode 114 is oxidized. If the "drain" micro-  
15 electrode 112 is moved to the negative of the source 114,  
current does not flow because the polyaniline remains  
insulating. Device 110 is not an exact analogue of a  
solid state diode because it is not a two-terminal device  
as is a p-n junction or a metal/semiconductor Schottky  
20 barrier. The diode-like behavior of device 110 results  
from a chemical reaction of the polymer 116 at a  
particular potential that causes a change in conductivity  
of the polymer 116.

25 Persistent diode-like behavior is obtained by  
maintaining one microelectrode, the drain 112, at a

1 negative potential at which it is insulating.  
Difficulties are encountered with degradation of the  
polyaniline when the potential of the microelectrode is  
held at a potential positive enough for the polyaniline to  
5 be insulating, +0.7 V vs. SCE, with the other  
microelectrode at a more negative potential.

Chemical-based devices depend on chemical  
reactions such as redox reactions which occur relatively  
slowly compared to the turn on/turn off speeds for solid  
10 state diodes and transistors. As shown in Fig. 16, device  
110 can be turned on and off in less than one second. In  
Fig. 16, the value of  $I_D$  is shown for a potential step of  
 $V_6$  from -0.2 to +0.3 V vs. SCE then back to -0.2 V vs. SCE  
at  $V_D$  of 0.18 V. By monitoring the rise and fall of  $I_D$  of  
15 the potential steps, on to off times of less than 50 ms  
and slightly longer off to on times were shown.

The polyaniline-coated device 110 exemplifies  
the type of molecule-based devices that could be used as  
chemical sensor where the input signal to the device is a  
20 redox agent that can equilibrate with the polyaniline 116  
to change the value of  $I_D$  at a given value of  $V_D$ . The  
specificity of the device stems from the fact that only  
those redox reagents that will bring the electrochemical  
potential of the polyaniline to a value that will allow  
25 current to pass will be detected. Further specificity

1 arises from the failure of the polyaniline to react with a  
particular given redox reagent. For example, polyaniline  
does not equilibrate with the  $H^+/H_2$  redox couple. There  
is, however, rapid equilibration of polyaniline with one-  
5 electron outer-sphere redox reagents such as  
 $Ru(NH_3)_6^{3+/2+}$ ,  $E^{0'}$  approximately equal to  $-0.18$  V vs. SCE  
which is close to the  $E^{0'}$  of  $H^+/H_2$  at  $pH=1$  of  
approximately  $-0.3$  V vs. SCE.

Polyaniline also equilibrates with  
10  $Fe(CN)_6^{3-/4-}$ . For example, immersion of the polyaniline-  
based device 110 into a solution of aqueous  $0.5$  M  $NaHSO_4$   
containing the oxidant  $K_3[Fe(CN)_6]$ ,  $E^{0'}$  of  $[Fe(CN)_6]^{3-/4-}$   
approximately equal to  $+0.2$  V vs. SCE, turns the device  
"on". Immersion of the device into a solution of  $0.5$  M  
15  $NaHSO_4$  containing  $Ru(NH_3)_6^{2+}$  turns the device "off".

As depicted in Fig. 17, the change in resistance  
of the polyaniline with a change in electrochemical  
potential can be brought about by exteranlly connecting  
the polyaniline-connected microelectrode array 120 to a  
20 macroscopic indicator electrode 122 that will respond to  
reagents 124 other than outer-sphere reagents. When the  
indicator electrode 122 is platinum, the microelectrode  
array 120 can be equilibrated with  $H^+/H_2$  since platinum  
equilibrates with  $H^+/H_2$ .

1           The device 130 in Fig. 18 is useful in  
characterizing the device of Fig. 17 since the  
potentiostat 132 and counter-electrode 134 can be used to  
5           quantitatively establish the amount of charge that is  
necessary to turn on the device 130. This device differs  
from the device 110 shown in Fig. 12a by the presence of  
an additional polymer-coated microelectrode and because  
the source and drain float.

10           It is also possible to chemically functionalize  
the polymer directly, as by the deposition of a metal such  
as palladium or a metal oxide onto the polyaniline  
connecting the microelectrodes. Palladium provides a  
mechanism for equilibrating the polymer with  $H_2O/H_2$  and  
15            $O_2/H_2O$ .

20           The present invention may be embodied in other  
specific forms without departing from the spirit and scope  
thereof. These and other modifications of the invention  
will occur to those skilled in the art. Such other  
embodiments and modifications are intended to fall within  
25           the scope of the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A device comprising two closely spaced electrically conductive electrodes on an insulating substrate wherein the first electrode is overlaid with a first redox polymer and the second electrode is overlaid with a second redox polymer, wherein the redox potential of said second polymer is different from the redox potential of said first redox polymer.
2. The device of claim 1 wherein said first polymer and said second polymer are not electrically connected.
3. The device of claim 2 wherein said first polymer is reduced and said second polymer is oxidized.
4. The device of claim 3 wherein said device is electrically charged to reduce the first polymer and oxidize the second polymer and wherein said device is useful as an energy storage device.
5. The device of claim 1 wherein said first redox polymer and said second redox polymer are electrically connected by a third polymer, said third polymer reversibly responding to a chemical signal.

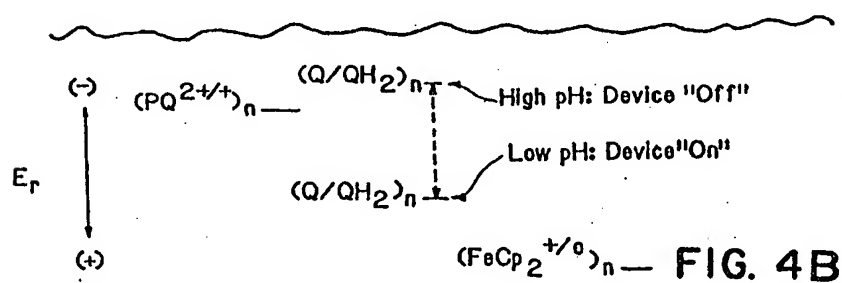
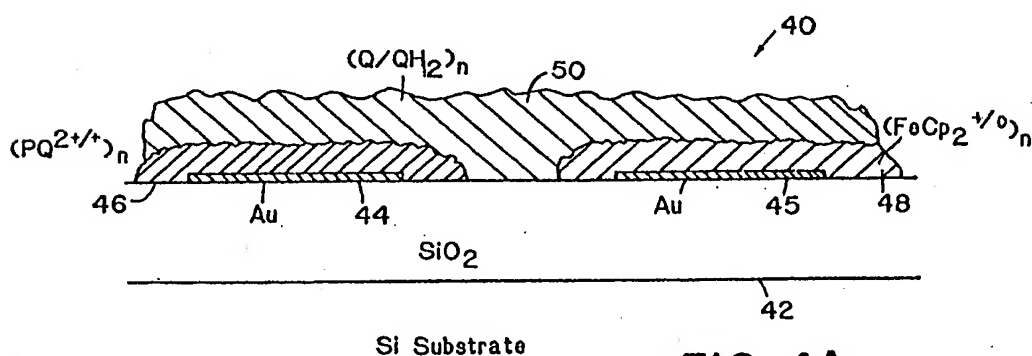
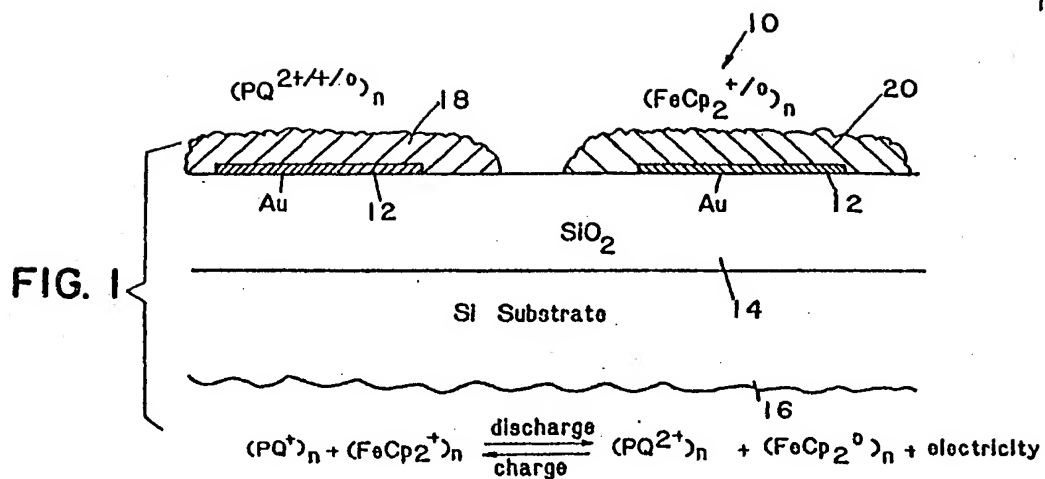
6. A triode-like device comprising at least two closely spaced electrodes on an insulating substrate overlaid with an electroactive polymer, wherein said polymer is insulating at a first redox potential, conducting at a second more positive redox potential, and insulating at a third, more positive redox potential.

7. The device of claim 6 wherein said polymer is polyaniline.

8. The device of claim 6 wherein said polymer is responsive to one electron outer-sphere redox reagents.



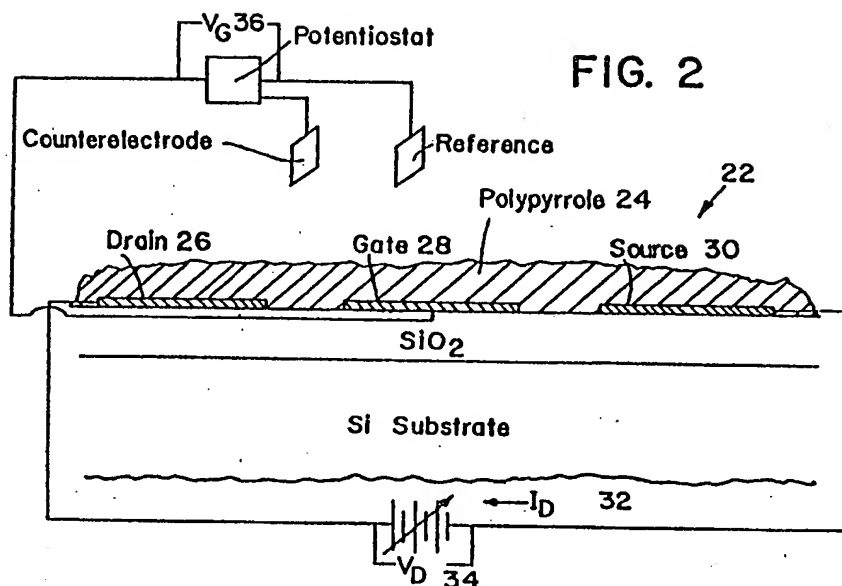
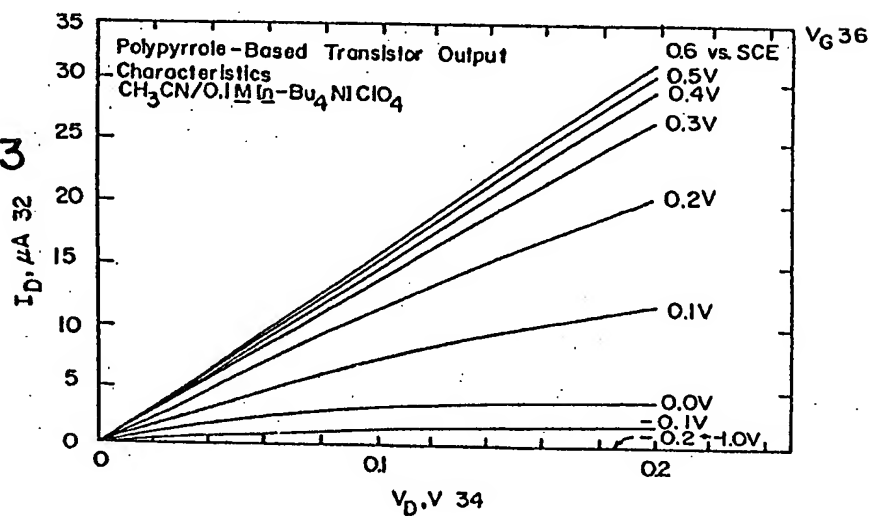
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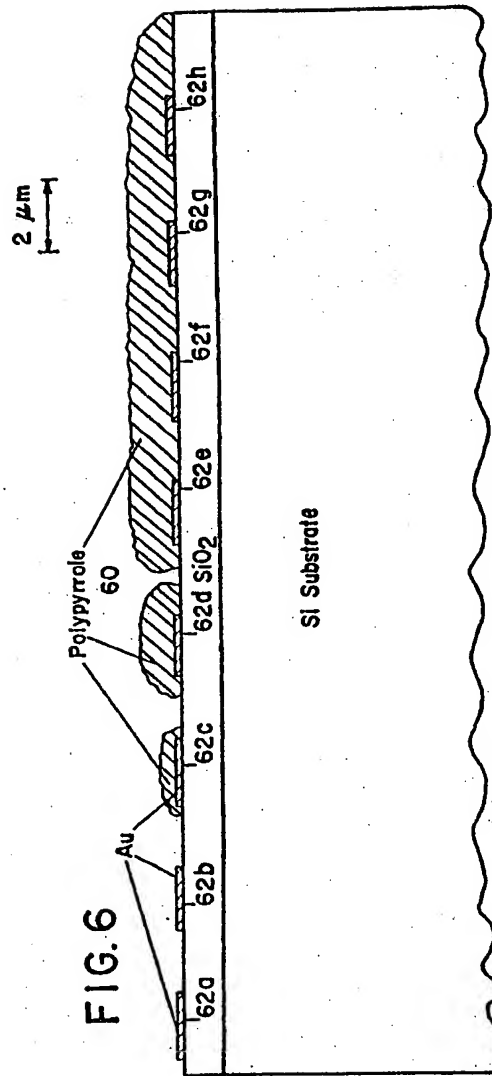
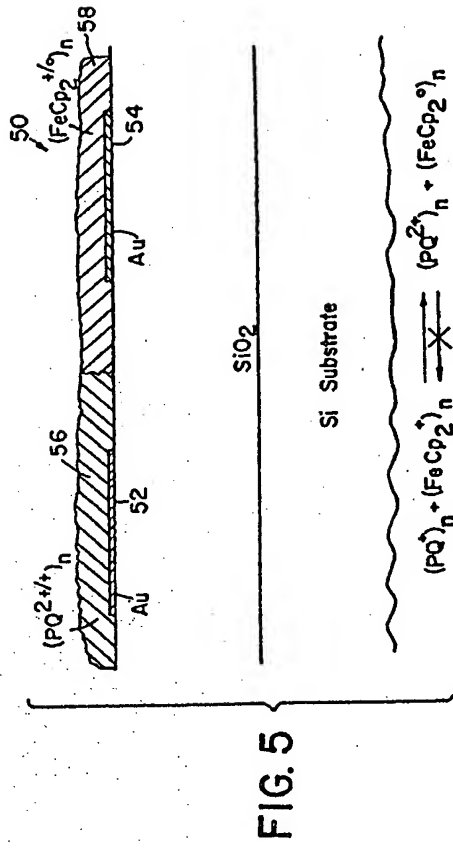


*James M. L. ...*



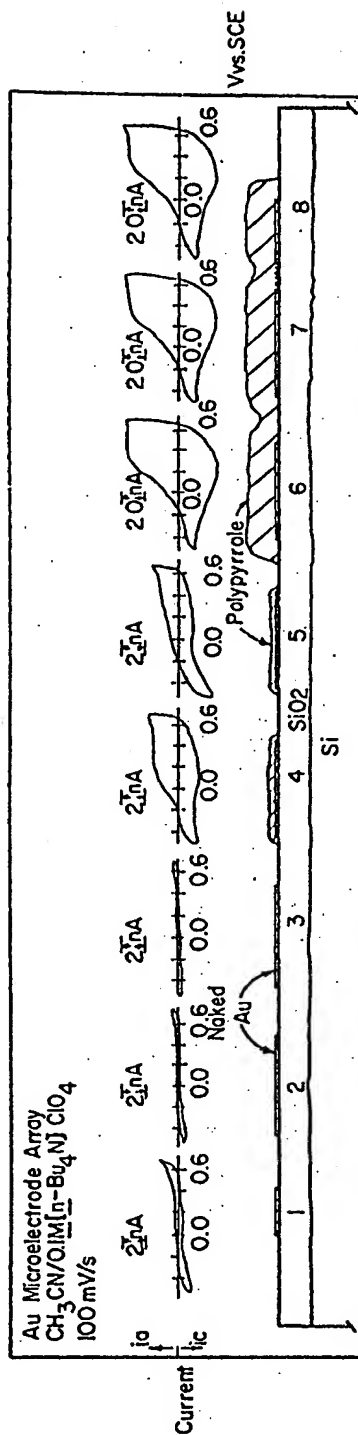
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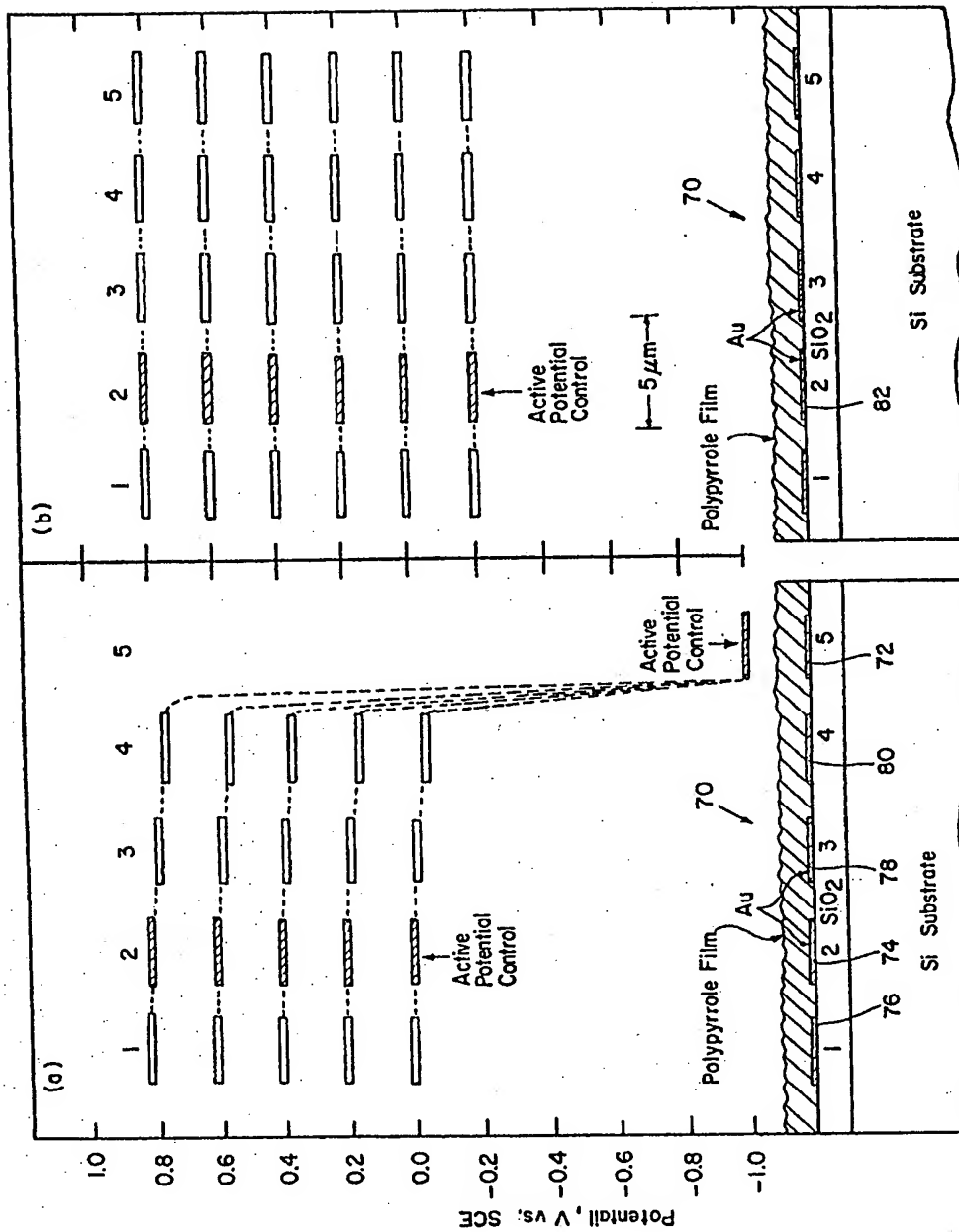
**FIG. 3***Robert M. Waymouth*



*James M. Mayer & Associates*

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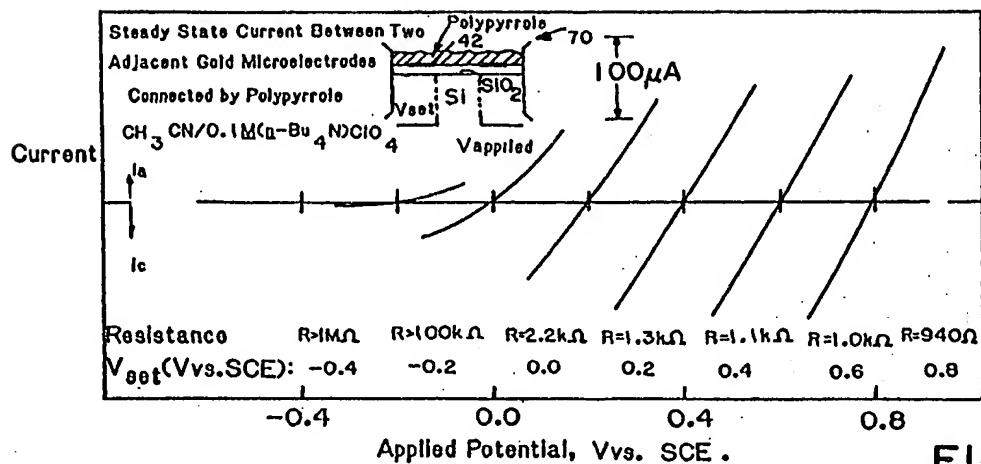


FIG. 9

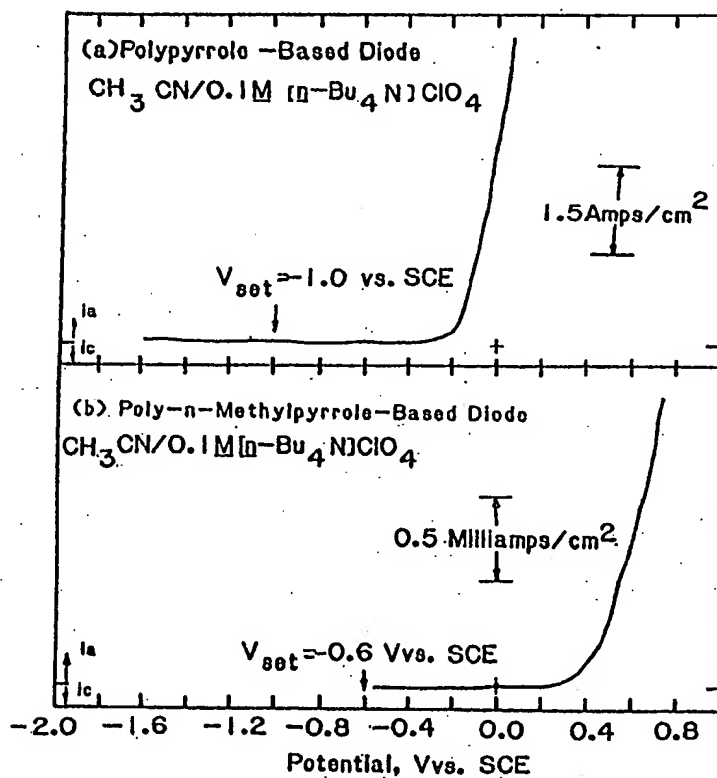


FIG. 10A

FIG. 10B

*Robert M. Waymouth & Richard H. Holm*



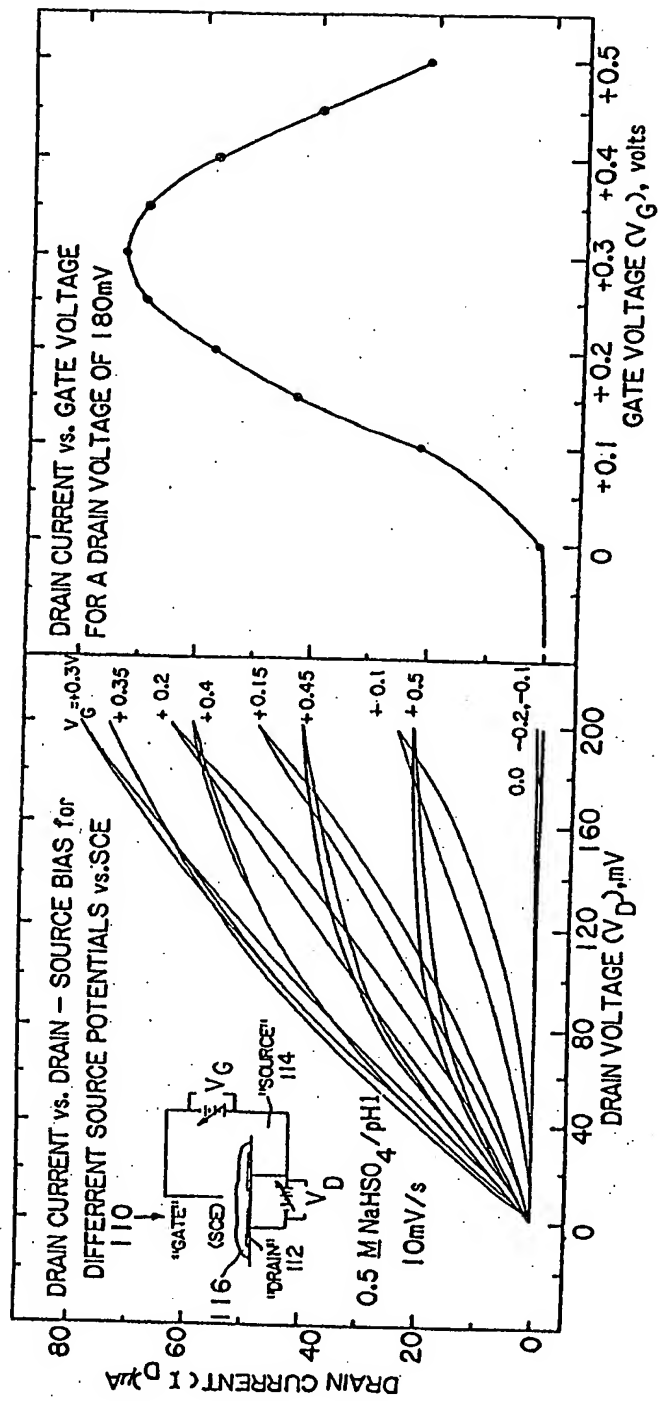


FIG. 12A

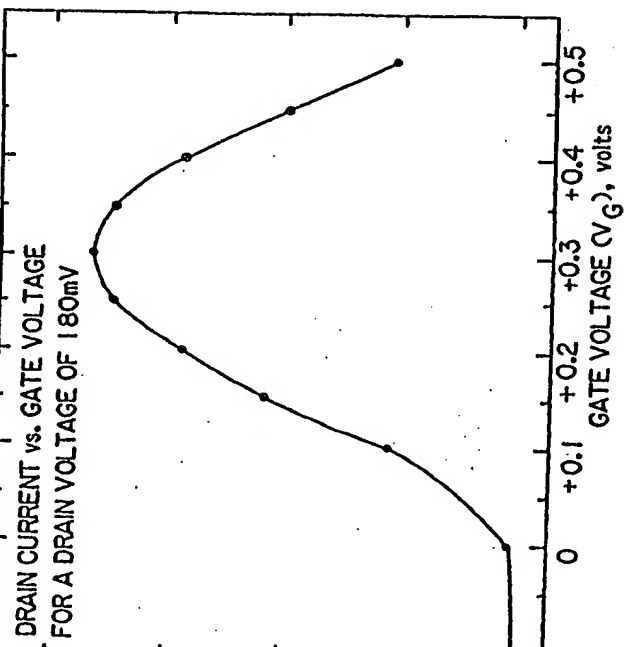


FIG. 12B

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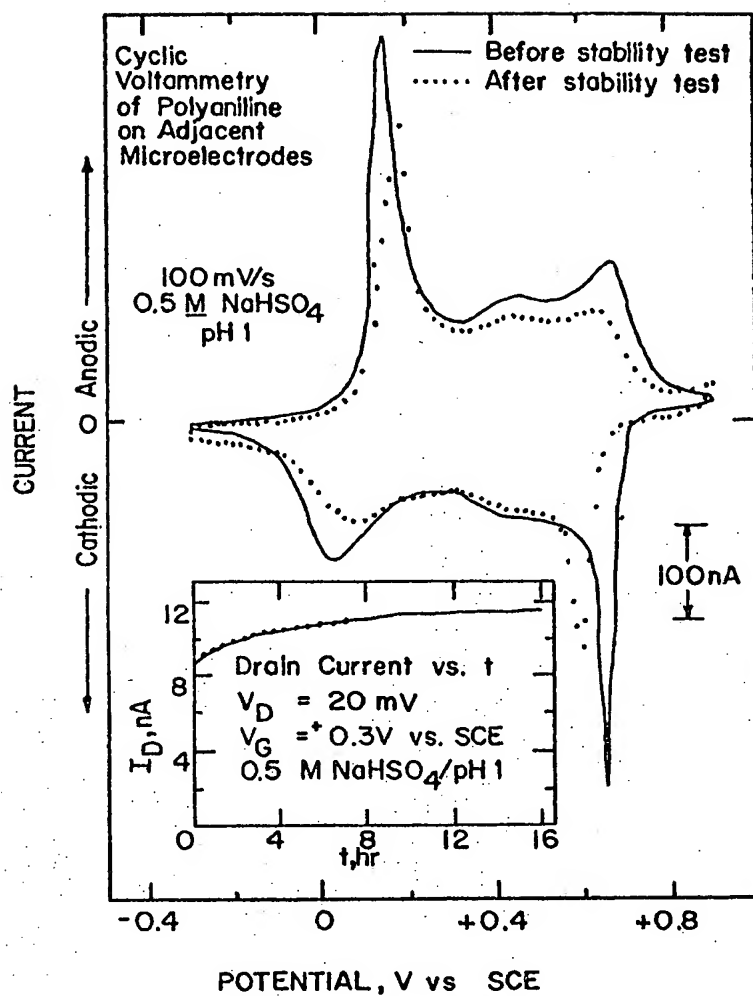


FIG. 13

*John M. Mayer*



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FIG. 14A

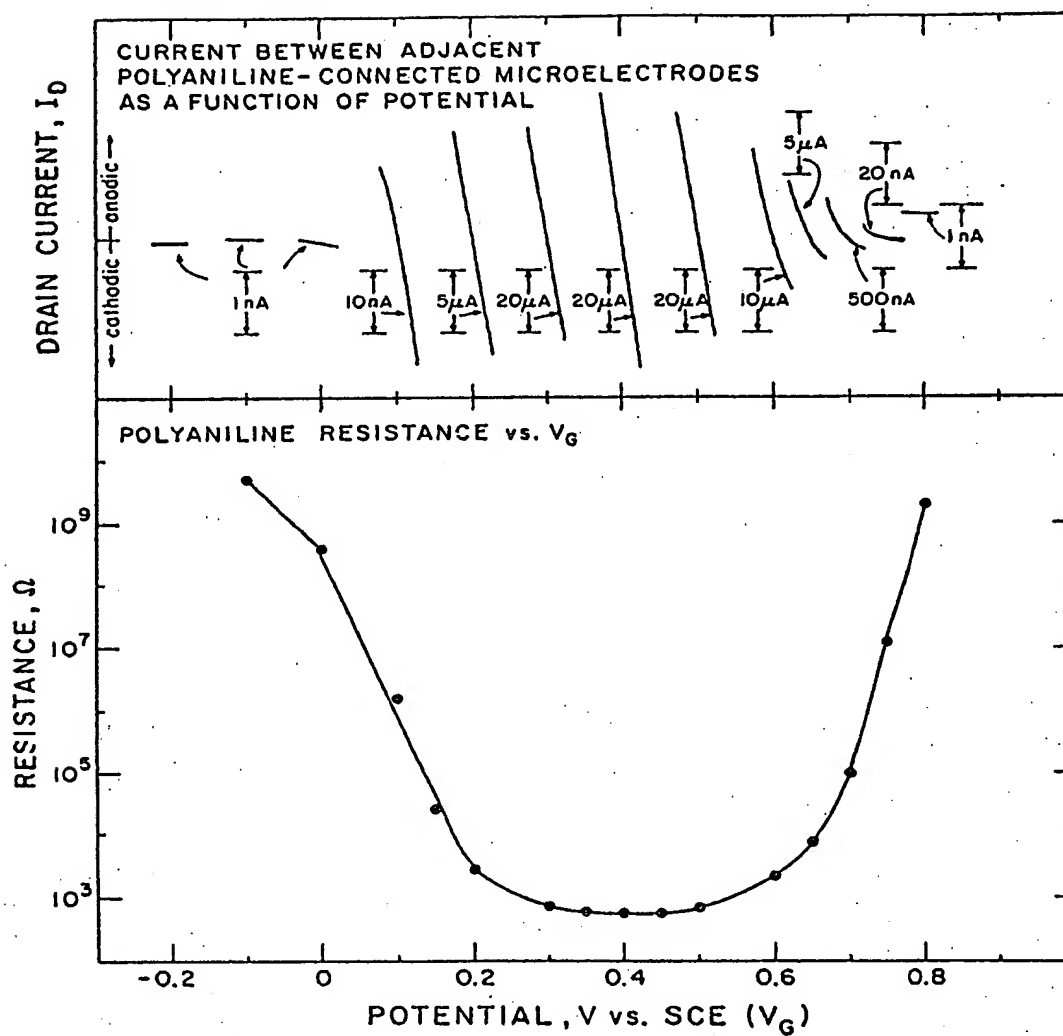


FIG. 14B

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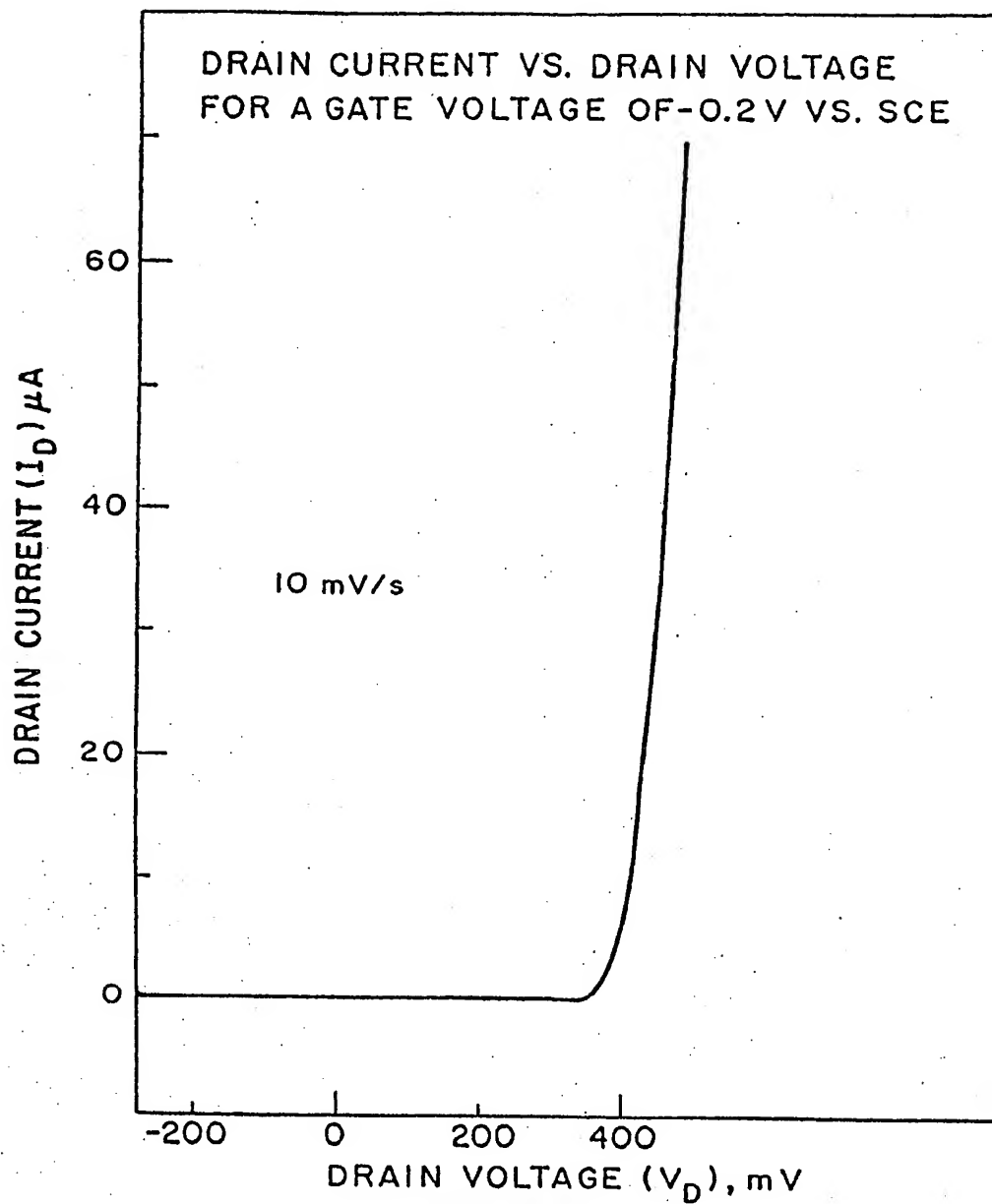
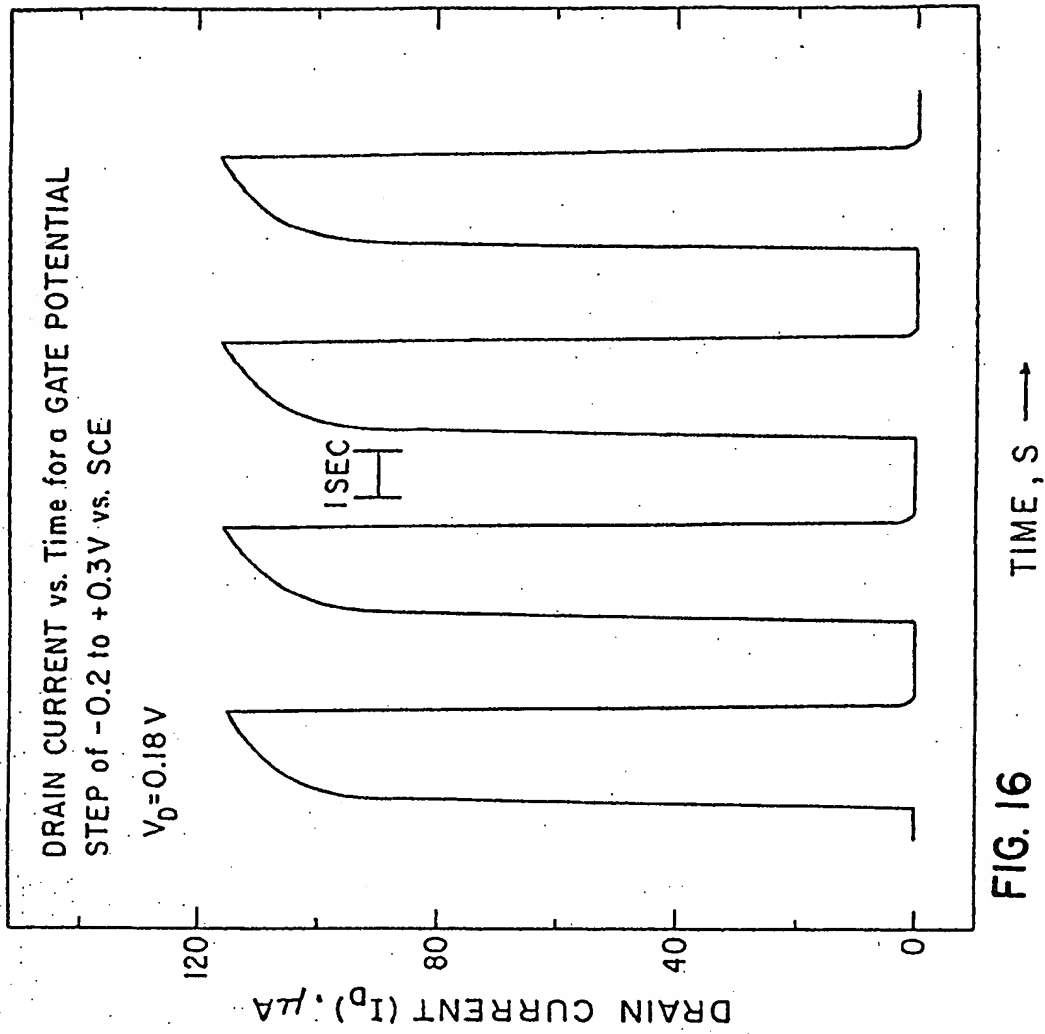


FIG. 15

12-12

*R. L. McLaughlin*

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